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**(54) Electrode and process for forming an electrode material**

Elektrode und Verfahren zur Herstellung eines Elektrodenmaterials

Electrode et procédé de fabrication d'un matériau d'électrode

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(56) References cited:  
**EP-A- 0 076 659** **DE-A- 3 729 033**  
**FR-A- 2 392 481** **US-A- 4 810 289**

• **PATENT ABSTRACTS OF JAPAN vol. 3, no. 50**  
**(C-44) 27 April 1979 & JP-A-54 026 220**  
**(MATSUSHITA) 27 February 1979**  
• **PATENT ABSTRACTS OF JAPAN vol. 13, no. 317**  
**(E-789) (3665) 19 July 1989 & JP-A-01 086 424**  
**(TOSHIBA) 31 March 1989**

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**EP 0 622 816 B1**

**Description****BACKGROUND OF THE INVENTION****1. Field of The Invention**

The present invention relates generally to a process for forming an electrode material to be assembled into a vacuum interrupter and to an electrode made of such an electrode material. Specifically, the present invention relates to such material composed of silver (Ag) and chromium (Cr) with low contact resistance and excellent breaking ability.

**2. Description of The Background Art**

Conventionally, copper(Cu)-bismuth(Bi) alloy is utilized for an electrode material of a vacuum interrupter. Such electrode material made of Cu-Bi generally contains less than 1 wt% of Bi against the amount of Cu, which is a basis metal, to increase welding proof of the material. Cu-Bi alloy has low contact resistance appropriate for electrodes which can provide large current. However, the material has certain problem in voltage resistance and breaking ability thereof.

Copper(Cu)-chromium(Cr) alloy in which Cr particles dispersing in a Cu matrix is also utilized for the material for the aforementioned usage because of superior voltage resistance and breaking ability thereof to Cu-Bi alloy. However, contact resistance of the alloy is relatively higher than that of Cu-Bi alloy, specifically, contact resistance significantly increases when current is broken.

In addition, electrode materials containing silver(Ag) is also known in the art, however, breaking ability thereof is inferior to that of Cu-Cr alloy or Cu-Bi alloy. Therefore, application of Ag containing material is limited as Ag-WC alloy for switches which are not frequently suffered from current breaking.

Recently, according to improvement of the vacuum interrupter, electrode materials with low contact resistance having superior voltage resistance and breaking ability to those of materials made of Cu-Bi alloy are more and more required for the electrode which can provide large amount of current.

US-A-4 810 289 discloses a process of hot isostatic pressing of powders to form electrical contacts, comprising the steps of: mixing powders selected from metals consisting of Ag, Cu, and mixtures thereof, with powders selected from the class consisting of CdO, W, WC, Co, Cr, Ni, C, and mixtures thereof; uniaxially pressing the powders without heating to a theoretical density of from 60 % to 95 %, to provide a compact; and hot isostatic pressing the compacts through a pressure transmitting container, at a pressure between 352 kg/cm<sup>2</sup> and 2,115 kg/cm<sup>2</sup> and at a temperature from 0.5°C to 100°C below the melting point or decomposition point of the lower melting powder, to provide simultaneous hot-pressing and densification to over 98% of theoretical density. The powders selected from the metals consisting of Ag, Cu, and mixtures thereof can constitute from 10 wt.% to 95 wt.% of the powder mixture.

DE-A-3 729 033 discloses a process for forming an electrode wherein powders from metals selected from the group consisting of Cu and Ag and powders from the class selected from the group consisting of Cr, Co, Fe, Mo, W, Ta and Ni are mixed and wherein the powders of the second group can constitute from 50 to 90 wt% of the powder mixture. This process, too, comprises a hot isostatic pressing step.

**SUMMARY OF THE INVENTION**

It is therefore a principal object of the present invention to provide a process for forming an electrode material which is assembled into a vacuum interrupter having low contact resistance and excellent voltage resistance with high breaking ability.

In order to accomplish the aforementioned and other objects and in accordance with the invention, a process for forming an electrode is composed of the steps defined in claim 1.

Ag powder may be contained between 50 to 95 wt% and Cr powder may be contained between 5 to 50 wt% in the blended powder.

Particle size of the Cr powder to be blended may be less than 150 μm, more preferably, less than 60 μm.

The electrode in accordance with the invention is defined in claim 4.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The present invention will be understood more fully from the detailed description given herebelow and from the accompanying drawings of the preferred embodiments of the invention. However, the drawings are not intended to imply limitation of the invention to a specific embodiment, but are for explanation and understanding only.

In the drawings:

Fig. 1 is a schematic cross-sectional view showing a structure of an electrode;

Fig. 2 is a graph showing a relationship between Cr contents and contact resistance of Ag-Cr and Cu-Cr electrodes;

Fig. 3 is a graph showing a relationship between breaking frequency and contact resistance of Ag-Cr and Cu-Cr electrodes;

Fig. 4 is a photograph showing a cross-sectional metallic structure of an 80wt%Ag-20wt%Cr electrode after current breaking;

Fig. 5 is a photograph showing a cross-sectional metallic structure of an 80wt%Cu-20wt%Cr electrode after current breaking;

Fig. 6 is a graph showing a relationship between Cr contents and breaking current of the electrode;

Fig. 7 is a photograph showing a cross-sectional metallic structure of a Ag-Cr electrode containing 100  $\mu\text{m}$  particle size of Cr after sintering;

Fig. 8 is a photograph showing a cross-sectional metallic structure of a Ag-Cr electrode containing 60  $\mu\text{m}$  particle size of Cr after sintering;

Fig. 9 is a photograph showing a cross-sectional metallic structure of a Ag-Cr electrode containing 10  $\mu\text{m}$  particle size of Cr after sintering;

Fig. 10 is a graph showing a relationship between Cr contents and welding force of electrodes containing various particle sizes of Cr;

Fig. 11 is a graph showing a relationship between Cr particle size and breaking ability of the electrode;

Fig. 12 is a photograph showing a cross-sectional metallic structure of a Ag-Cr electrode containing 10  $\mu\text{m}$  particle size of Cr after current breaking;

Fig. 13 is a photograph showing a cross-sectional metallic structure of a Ag-Cr electrode containing 100  $\mu\text{m}$  particle size of Cr after current breaking; and

Fig. 14 is a photographic view comparing metallic structures between an electrode base and an electrode surface of a Cu-20wt%Cr electrode after current breaking.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

In the present invention, silver(Ag) powder, which is considered to promote reduction of contact resistance of electrodes, was utilized in variable compositions in the form of Ag-Cr electrodes. As a process for forming the electrodes, powder metallurgy, i.e., compacting and forming metallic powder then sintering, was used. The process utilizing powder metallurgy has been known in the art as that which can reduce manufacturing cost (refer to Japanese Patent First Publication (not allowed) No.53-149676).

## EXAMPLE 1

Chromium(Cr) powder having particle size of less than 150  $\mu\text{m}$  and Ag powder having that of less than 80  $\mu\text{m}$  were blended in variable ratios as shown in Table 1. The blended powder was filled into a die and compacted under the pressure of 3.5 ton/cm<sup>2</sup>. Then, the compacted body was heated to sinter under vacuum condition ( $5 \times 10^{-5}$  Torr) at 950 °C, which is a temperature around melting point of Ag, for 2 hours to obtain an ingot for an electrode. Density of each ingot obtained is also shown in Table 1. As a comparison, 20%Cr-80%Cu was prepared by a process similar to that of the aforementioned. Table 1 shows conductivity of each compacted body when utilized as the electrode and density ratio thereof.

Table 1

No.	Composition wt%		Conductivity IACS%	Density Ratio %
	Ag	Cr		
1	95	5	97	99
2	90	10	85	99
3	80	20	70	97
4	70	30	55	95
5	60	40	45	94
6	50	50	35	91
7	20Cr -80Cu		50	95

According to microphotographic observation of each ingot, Cr particles were evenly dispersed in a Ag matrix.

The ingot was formed into an electrode, then assembled into an vacuum interrupter to measure contact resistance of the electrode (refer to Fig. 1, wherein numeral 1 designates an electrode and numeral 2 designates a lead). Contact resistances of each electrode are shown in Fig. 2 with that of Cu-Cr electrode as a comparison. In the figure, maximum values of contact resistances during current breaking until 20 KA are plotted. Contact resistance of Ag-Cr electrodes were effectively reduced compared to that of the Cu-Cr electrode.

Fig. 3 shows a relationship between breaking frequency and contact resistance of the 80wt%Ag-20wt%Cr electrode and the 80wt%Cu-20wt%Cr electrode. Breaking test was done under the conditions shown in the horizontal axis of the figure. Referring to Fig. 3, the electrode of 80wt%Ag-20wt%Cr shows significantly lower contact resistance than that of the comparison(i.e., 80wt%Cu-20wt%Cr electrode) even though electric current was repeatedly broken.

Fig. 4 shows a metallic structure of the electrode of 80wt%Ag-20wt%Cr after current breaking, and Fig. 5 shows that of the electrode of 80wt%Cu-20wt%Cr. Both are microscopic photographs. As shown in Fig. 5, the surface of the Cu-Cr electrode is covered with a molten layer A having metallic structure where less than 0.5  $\mu$ m particle size of Cr particles being evenly dispersed. This seems to be derived from immediate cooling of an even liquid phase containing Cu and Cr which is formed when the electrode is molten by current breaking energy. Therefore, the electrode surface shows good hardness due to even dispersion of Cr. This causes increase of contact resistance of the electrode. On the other hand, the electrode of Ag-Cr, as shown in Fig. 4, has no layer showing distinct dispersion of Cr particles, though a molten layer A is shown adjacent the electrode surface. Cr particles and Ag matrix are unevenly located. Therefore, increase of contact resistance of the Ag-Cr electrode can be reduced.

Accordingly, Ag-Cr alloy is prefer to apply for the electrode having lower contact resistance. Additionally, from Table 1 and Figs. 2 and 3, 50 to 95 wt% contents of Ag and 5 to 50 wt% contents of Cr are prefer to be blended.

## EXAMPLE 2

Ag powder having particle size of less than 80  $\mu$ m and Cr powder having that of less than 150  $\mu$ m were blended in various content ratios shown in Table 2.

Table 2

No.	Composition wt%		Conductivity IACS%	Density Ratio %
	Ag	Cr		
1	95	5	97	99
2	90	10	85	99
3	85	15	80	98
4	80	20	70	97
5	70	30	55	95
6	60	40	45	94
7	50	50	35	91

Then, the blended powder was filled in a die, pressed under 3.5 ton/cm<sup>2</sup> to obtain a compacted body having 85 mm of diameter. The obtained bodies were formed into ingots for electrodes by the similar process under the similar conditions to the above-mentioned example 1. Conductivity and Density ratio of each ingots are also shown in Table 2.

Then, each ingot was formed in an electrode having a spiral configuration of 80 mm diameter and assembled into a vacuum interrupter to measure current breaking ability thereof. Results are shown in Fig. 6(a curve indicated by 100  $\mu$ m). Contact resistance of the electrode of Ag-Cr shows lesser increase compared to that of the Cu-Cr electrode even though current breaking is repeatedly performed. Fig. 7 is a microphotograph showing metallic structure of the electrode of the present example.

## EXAMPLE 3

Ag powder having particle size of less than 80  $\mu$ m and Cr powder having that of less than 60  $\mu$ m were blended in various content ratios shown in Table 3.

Table 3

No.	Composition wt%		Conductivity IACS%	Density Ratio %
	Ag	Cr		
1	95	5	94	98
2	90	10	80	97
3	85	15	75	97
4	80	20	62	95
5	70	30	48	92
6	60	40	45	94

Then, the blended powder was filled in a die, pressed under 3.5 ton/cm<sup>2</sup> to obtain a compacted body having 85 mm of diameter. The obtained bodies were formed into ingots for electrodes by the similar process under the similar conditions to the above-mentioned example 1. Conductivity and Density ratio of each ingots are also shown in Table 3.

Then, electrodes were made by the similar process under the similar conditions to the above-mentioned example 2. Results are shown in Fig. 6(a curve indicated by 60  $\mu$  m). Contact resistance of the electrodes of Ag-Cr shows lesser increase compared to that of the Cu-Cr electrode even though current breaking is repeatedly performed. Fig. 8 is a microphotograph showing metallic structure of the electrode of the present example.

#### EXAMPLE 4

Ag powder having particle size of less than 80  $\mu$  m and Cr powder having that of less than 10  $\mu$  m were blended in various content ratios shown in Table 4.

Table 4

No.	Composition wt%		Conductivity IACS%	Density Ratio %
	Ag	Cr		
1	95	5	92	96
2	90	10	78	95
3	85	15	65	90
4	80	20	50	87
5	70	30	45	85

Then, the blended powder was filled in a die, pressed under 3.5 ton/cm<sup>2</sup> to obtain a compacted body having 85 mm of diameter. The obtained bodies were formed into ingots for electrodes by the similar process under the similar conditions to the above-mentioned example 1. Conductivity and Density ratio of each ingots are also shown in Table 4.

Then, electrodes were made by the similar process under the similar conditions to the above-mentioned example 2. Results are shown in Fig. 6(a curve indicated by 10  $\mu$  m). Contact resistance of the electrodes of Ag-Cr shows lesser increase compared to that of the Cu-Cr electrode even though current breaking is repeatedly performed. Fig. 9 is a microphotograph showing metallic structure of the electrode of the present example.

Fig. 10 shows a relationship between welding force of the electrode of the aforementioned three examples and Cr contents thereof. Welding force of the Cu-Cr electrode is also shown as a comparison.

According to the aforementioned examples, the Ag-Cr electrodes show lesser increase of contact resistance after current breaking. In addition, contact resistance of the electrode does not depend upon Cr particle size contained therein, but increases according to contents of Cr is increased. However, contact resistance of the electrode is not increased by current breaking. Further to say, the Ag-Cr electrode shows excellent welding ability compared to the electrode made of Cu-Cr.

Generally, current breaking ability of the electrode having smaller particle size of Cr is superior to that having larger one. If Cr particle size becomes larger, arc generated at contact points of Cr and Ag particles tends to be trapped in the Cr particle to prevent smoothly arc migration. On the other hand, if Cr particle size becomes smaller, arc can be rapidly migrated because arc is not trapped in the Cr particle. This allows current breaking to be rapidly performed. Fig. 11 shows a relationship between current breaking ability of the electrode and Cr particle size thereof. Referring to Figs. 11 and previously referred 10, less than 60  $\mu$  m of Cr particle size is prefer to maintain breaking ability of the electrode.

Figs. 12 and 13 are microphotographs showing cross-sectional metallic structures of the electrodes obtained from Examples 4 and 2 after current breaking. Referring to the figures, metallic structure becomes uneven when Cr particle size is larger, therefore, contact portions of Cr and Ag particles are decreased. This causes partial evaporation of Ag or peeling of material from the electrode surface to induce irregularity thereof. On the other hand, if Cr particle size is smaller, any inconveniences as the aforementioned do not occur, therefore, metallic structure adjacent the electrode surface becomes even after current breaking.

Fig. 14 shows metallic structure of the Cu-Cr electrode as a comparison of the Ag-Cr electrode having small Cr particle size which is shown in Fig. 11. A molten layer in which Cr particle having less than  $0.5\ \mu\text{m}$  particle size is dispersed is shown adjacent the surface of the Cu-Cr electrode. A liquid phase wherein Cr and Cu particles are evenly dispersed is formed when the electrode is molten by energy of current breaking. The molten layer shown adjacent the electrode surface seems to be formed by immediate cooling of such liquid phase. Thus, hardness of the electrode increases by even dispersion of Cr particles to cause contact resistance of the electrode to be increased.

According to examples 2 to 4, 5 to 50 wt% of Cr powder having less than  $60\ \mu\text{m}$  of particle size and 50 to 95 wt% of Ag powder are prefer to be blended for the electrode material of the vacuum interrupter. The blended powder is compacted, sintered under the temperature around melting point of Ag. Density of the article is preferably regulated to at least 90 %.

Temperature to sinter the compacted body of the electrode material is preferably determined in the range between 800 to 950 °C which are the temperatures around melting point of Ag. When the temperature does not exceed 800 °C, sintering of the compacted body cannot be promoted. On the other hand, when that exceeds 950 °C, partial melting of the electrode or surface deformation thereof (e.g., blisters) tends to be caused.

Electrode density is required to be more than 90%, because when that does not exceed 90%, conductivity of the electrode is deteriorated. In addition, sintering thereof becomes not sufficient. This causes deterioration of the electrode strength.

Therefore, the vacuum interrupter having lower contact resistance than that using the Cu-Cr electrode can be obtained because the ratio of Ag powder and Cr powder, temperature for sintering, and electrode density are thus specified, contact resistance of the electrode does not increase even though current breaking is repeatedly done.

In addition, the electrode of the present invention shows good breaking ability superior to that of the Ag-WC electrode and low contact resistance compared to that of the Cu-Cr electrode.

Furthermore, the electrode of the present invention shows good welding ability, size of a breaker assembled into the interrupter can be reduced because tripping force applied thereon can be reduced. Therefore, the breaker can be provided at a low cost even though Ag which has been known as a relative expensive material is used for the electrode.

Further to say, when the interrupter is made of the Cu-Cr electrode, principal conductor conventionally occupies large space in the interrupter, furthermore, a fin having good heat radiation is required, these cause size of the interrupter to be enlarged and cost for forming that to be increased. However, when that is made of the electrode material of the present invention, such problems can be solved.

While the present invention has been disclosed in terms of the preferred embodiment in order to facilitate better understanding of the invention, it should be appreciated that the invention can be embodied in various ways without departing from the scope of the invention as defined by the claims.

## Claims

1. A process for forming an electrode material which exhibits sufficiently reduced contact resistance comprising the steps of:

blending silver (Ag) powder and chromium (Cr) powder,  
wherein the content of said chromium powder is determined to be greater than or equal to 5 wt% and not exceeding 50 wt%,  
compacting said blended powder to compacted body,  
pressing said body at a pressure of  $3.5\ \text{ton/cm}^2$ ,  
sintering said body under vacuum condition at a temperature greater than or equal to 800°C and not exceeding 950°C, and  
regulating density of the sintered article at at least 90%, to restrain increase of contact resistance after repeated current breaking.

2. The process as set forth in claim 1, wherein the particle size of said Cr powder to be blended is less than  $150\ \mu\text{m}$ .

3. The process as set forth in claim 1, wherein the particle size of said Cr powder to be blended is less than  $60\ \mu\text{m}$ .

4. An electrode made of an electrode material, the electrode material being formed exclusively by means of the method according to anyone of claims 1 to 3.

5 **Patentansprüche**

1. Prozeß zum Bilden eines Elektrodenmaterials, das einen ausreichend verringerten Kontaktwiderstand aufweist, umfassend die Schritte:

10 Mischen von Silber(Ag)-Pulver und Chrom(Cr)-Pulver, wobei der Gehalt an Chrompulver mit größer als oder gleich 5 Gew.-% festgelegt ist und 50 Gew.-% nicht überschreitet,

Verdichten des gemischten Pulvers zu einem verdichteten Körper,

15 Pressen des Körpers bei einem Druck von 3,5 t/cm<sup>2</sup>,

Sintern des Körpers unter Vakuumbedingung bei einer Temperatur, die größer als oder gleich 800°C ist und 950°C nicht überschreitet, und

20 Regulieren der Dichte des gesinterten Artikels auf zumindest 90%, um einen Anstieg des Kontaktwiderstandes nach wiederholtem Unterbrechen eines Stromes zu hemmen.

2. Prozeß nach Anspruch 1, wobei die Partikelgröße des zu mischenden Cr-Pulvers kleiner als 150 µm ist.

25 3. Prozeß nach Anspruch 1, wobei die Partikelgröße des zu mischenden Cr-Pulvers kleiner als 60 µm ist.

4. Elektrode, die aus einem Elektrodenmaterial gefertigt ist, wobei das Elektrodenmaterial ausschließlich mittels des Verfahrens gemäß einem der Ansprüche 1 bis 3 gebildet wird.

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**Revendications**

1. Procédé de formation d'un matériau d'électrode qui présente une résistance de contact suffisamment réduite, comprenant les étapes de :

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mélanger de la poudre d'argent (Ag) et de la poudre de chrome (Cr) où la teneur en ladite poudre de chrome est déterminée pour être plus grande que ou égale à 5 % en poids et ne pas dépasser 50 % en poids, tasser ladite poudre mélangée en un corps tassé, presser ledit corps à une pression de 3,5 tonnes/cm<sup>2</sup>,

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fritter ledit corps en condition de vide à une température plus importante que ou égale à 800°C et ne dépassant pas 950°C, et

réguler la densité de l'article fritté à au moins 90 % pour restreindre une augmentation de la résistance de contact après interruption répétée du courant.

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2. Procédé selon la revendication 1 où la grandeur des particules de ladite poudre de Cr à mélanger est inférieure à 150 µm.

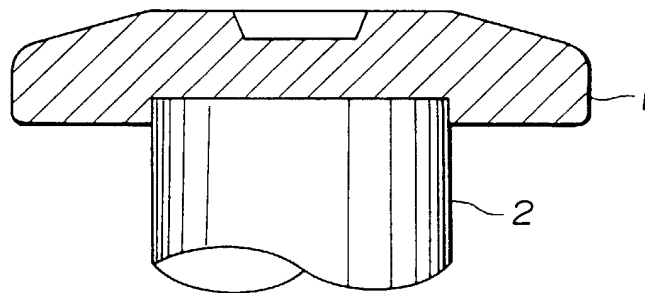
3. Procédé selon la revendication 1 où la grandeur des particules de ladite poudre de Cr à mélanger est inférieure à 60 µm.

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4. Electrode faite d'un matériau d'électrode, le matériau d'électrode étant formé exclusivement au moyen de la méthode selon l'une quelconque des revendications 1 à 3.

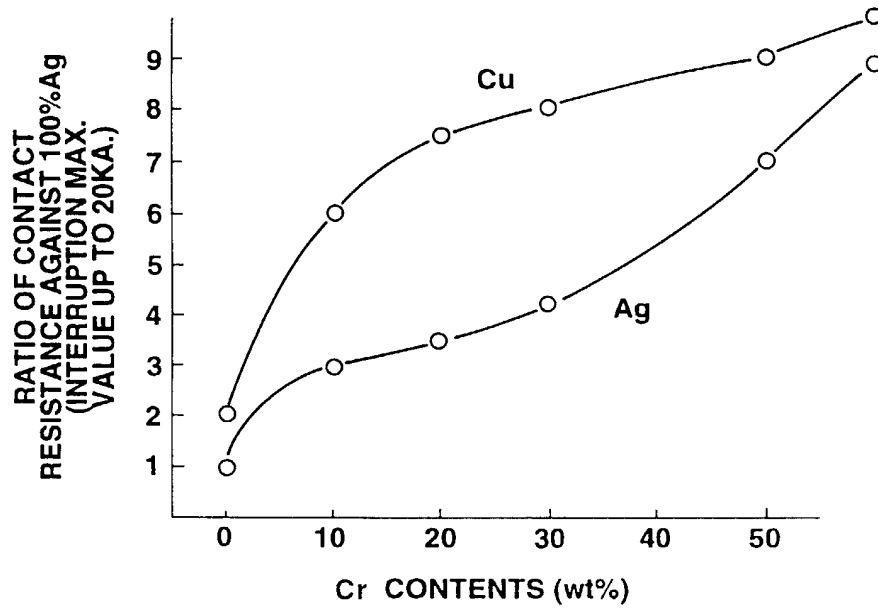
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FIG.1

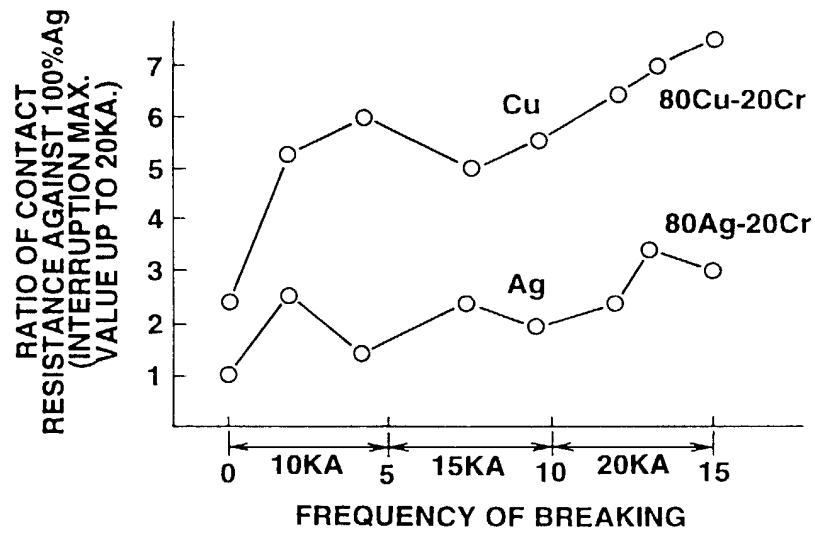




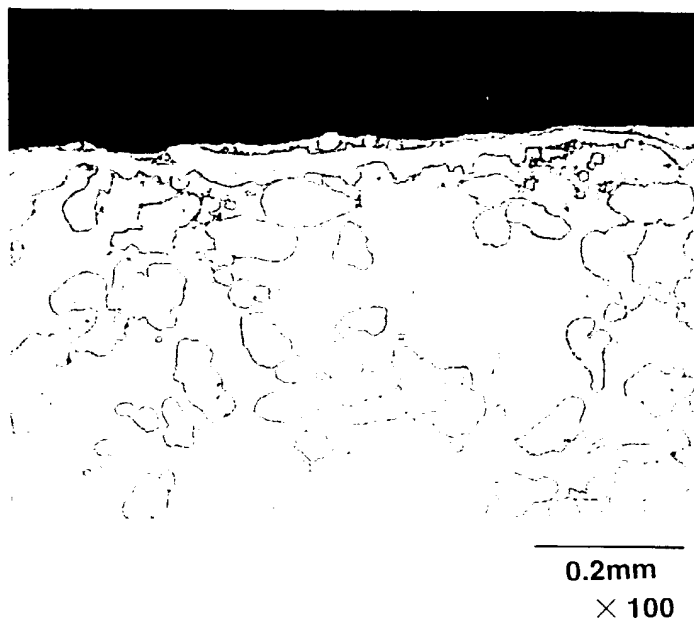
**FIG.2**



**FIG.3**



**FIG. 4**



**FIG. 5**

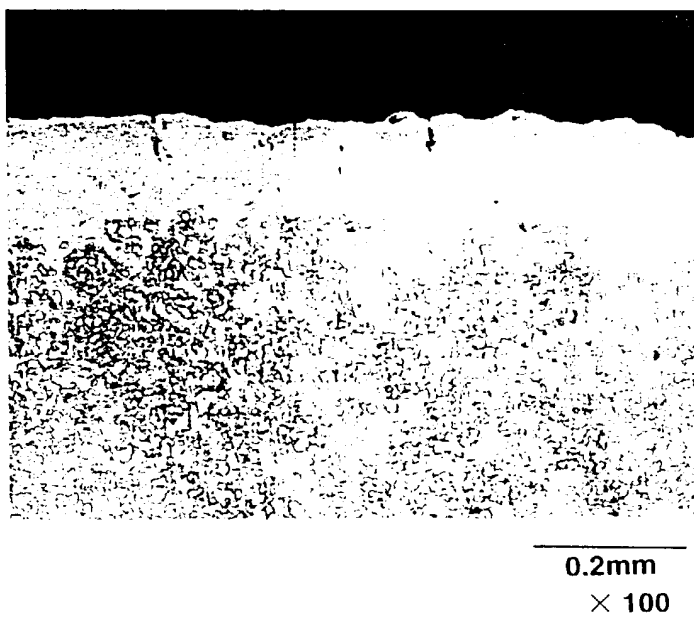
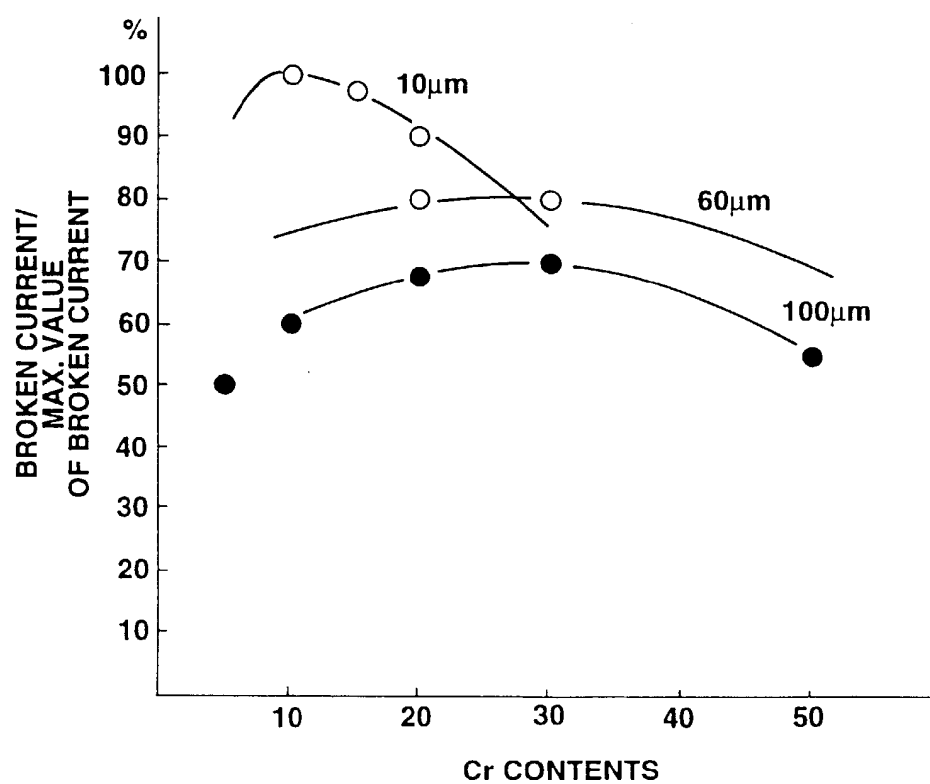
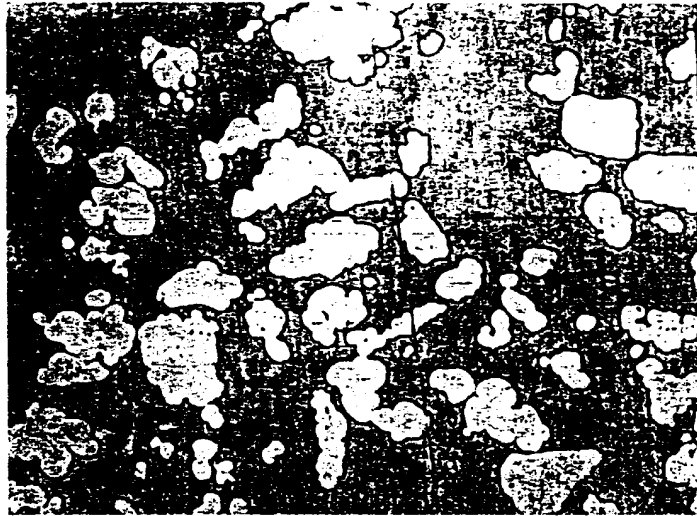


FIG.6

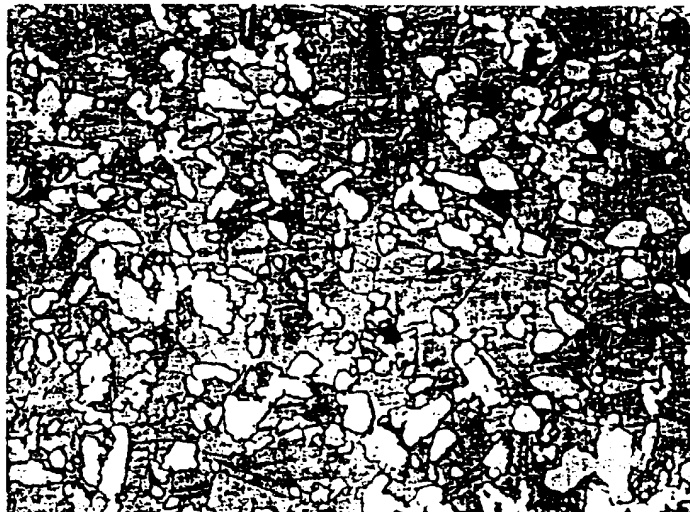


**FIG.7**



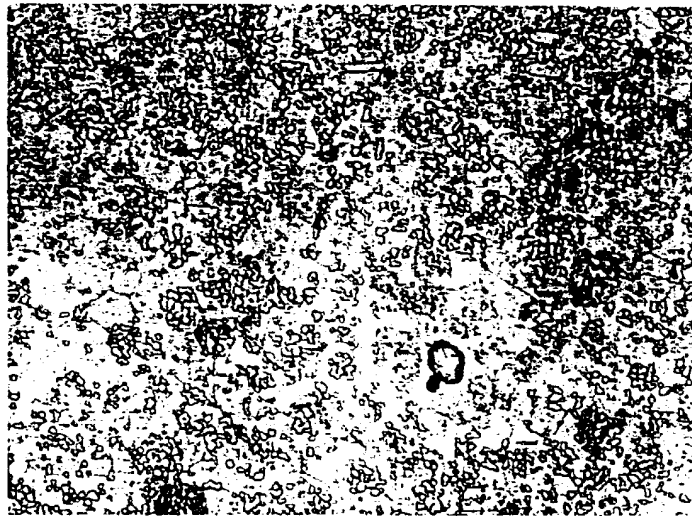
× 100

**FIG.8**

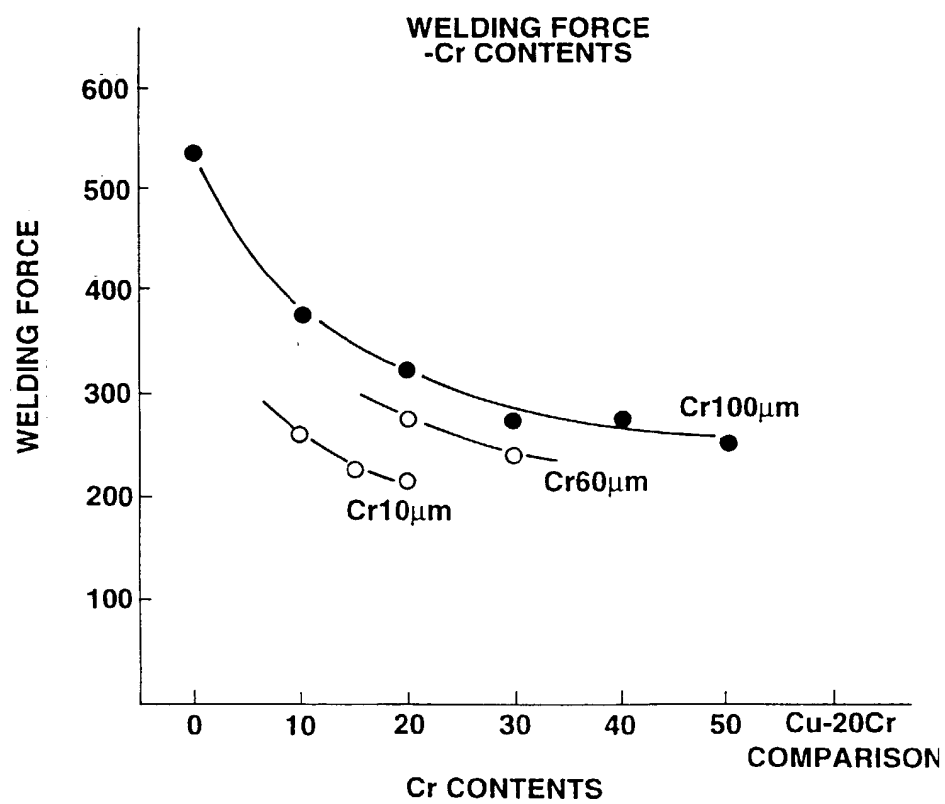


× 100

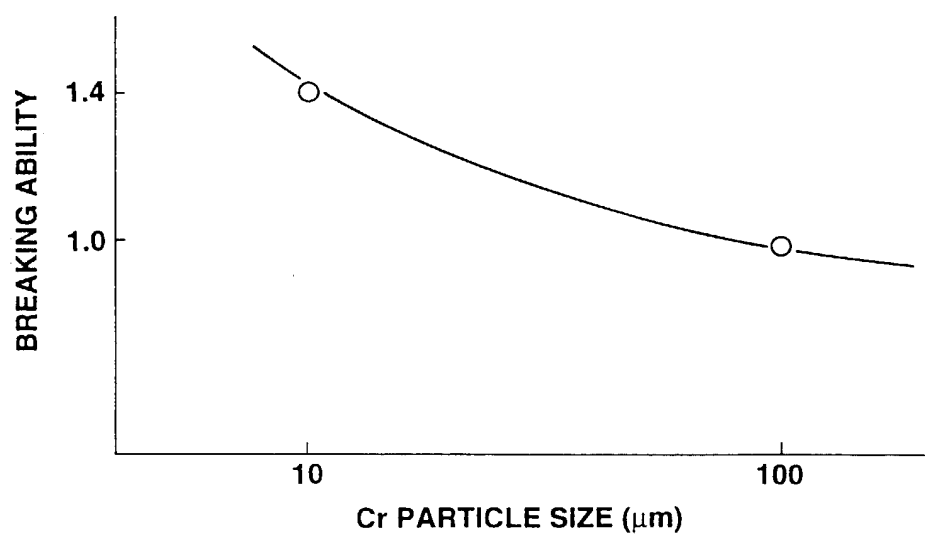
**FIG.9**



× 100

**FIG.10**

**FIG.11**



## FIG.12

PARTICLE SIZE OF Cr-10  $\mu\text{m}$  ( $\times 100$ )

ELECTRODE  
SURFACE



## FIG.13

PARTICLE SIZE OF Cr-100  $\mu\text{m}$  ( $\times 100$ )

ELECTRODE  
SURFACE





**FIG.14**

**CROSS-SECTIONAL SURFACE  
OF Cu-20% Cr ATOMIZED ELECTRODE  
(AFTER LARGE CURRENT BREAKING)**

